

PALEOCLIMATIC ASSESSMENT OF CRETACEOUS LACUSTRINE AND MARINE-EVAPORITIC SEQUENCES FROM THE POTIGUAR BASIN (BRAZIL) BASED ON THE HYDROGEN ISOTOPIC COMPOSITIONS OF SATURATED HYDROCARBONS

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ABSTRACT – Photoautotrophic organisms grown under laboratory and natural conditions synthesize lipids having hydrogen isotopic compositions depleted by about 150‰ compared with the water in the medium of growth. Once the hydrogen is bonded in the carbon the chances for exchange are highly reduced. Thus, lipids are transformed through diagenetic processes into saturated hydrocarbons that comprise a significant percentage of the bitumens and of oils. Considering that isotopic compositions of water reflect the climate in continental and transitional settings, paleoclimatic conditions can be assessed by inferring, at least roughly, the δD of the water in the paleoenvironment with the equation $\delta D_{sat} - \delta D_{water} \cong -150\text{‰}$. The stratigraphic variability of δD_{sat} in Cretaceous lacustrine shales from the Potiguar Basin is given by alternating intervals of lighter and heavier isotopic compositions, from -127 to -107‰, suggesting fluctuations in the hydrogen isotopic compositions of the paleolake due to periods of higher and lower aridity ($23 \leq \delta D_{water} \leq 43\text{‰}$) under warm and semi-arid conditions. The marine-evaporitic sequence is characterized by δD_{sat} values ranging from -157 to -110‰. Depletion in D increases from the base toward the top of that examined Alagamar Formation, suggesting the evolution of a lagoon under arid to semi-arid climates ($\delta D_{water} \cong 40\text{‰}$) to a more open and strongly marine-influenced conditions with δD_{water} close to that expected for the ocean. The observed maximal depletions in D possibly indicate, as expected, that mid-Cretaceous marine waters were, due to much lower global inventories of D-depleted ice, slightly depleted in D relative to modern ocean water. The estimated values of δD_{water} in the examined paleoenvironments are compatible with those found in modern environments under similar climatic conditions.

RESUMO – Os organismos fotoautotróficos sob condições de laboratório ou em ambiente natural sintetizam lipídeos com composição isotópica de hidrogênio depletada em torno de 150‰ em relação a água do meio de crescimento. As chances de troca isotópica do hidrogênio se tornam muito reduzidas após o mesmo se ligar ao carbono. Assim, os lipídeos são transformados, através de processos diagenéticos, em hidrocarbonetos saturados que compõem uma porcentagem significativa dos óleos e betumens. Considerando que as composições isotópicas da água refletem o clima nos ambientes continental e transicional, as condições paleoclimáticas podem ser inferidas pela estimativa, pelo menos aproximada, de δD da água no paleoambiente com a equação $\delta D_{sat} - \delta D_{water} \leq 150\text{‰}$. Os valores da composição isotópica de hidrogênio em hidrocarbonetos saturados (δD_{sat}) de folhelhos lacustres da Formação Pendência (Neocomiano) da Bacia Potiguar estão representados por valores alternados de composição isotópica mais leve ou mais pesada, de -127 a -107‰, sugerindo que as flutuações isotópicas de hidrogênio do paleolago foram devido a variações climáticas que correspondem a períodos de maior ou menor aridez ($23\text{‰} \leq \delta D_{water} \leq 43\text{‰}$), sob condições de clima semi-árido quente. A sequência marinho-evaporítica da Formação Alagamar (Aptiano) está caracterizada por valores de δD_{sat} variando de -157 a -110‰. A depleção em deutério aumenta da base em direção ao topo da seção estudada, sugerindo a evolução de uma laguna, sob condições de clima quente árido a semi-árido ($\delta D \cong 40\text{‰}$) para um ambiente com influência marinha significativa onde $\delta D_{água}$ estaria próximo aquele esperado para os oceanos. As depleções máximas em deutério possivelmente indicam que as águas marinhas do Cretáceo Inferior-Médio, devido a uma menor volume de gelo nas calotas polares, eram depletadas em deutério comparando-as com as águas dos oceanos modernos. Os valores estimados de $\delta D_{água}$ dos paleoambientes estudados são compatíveis com aqueles encontrados em ambientes análogos modernos, sob condições climáticas semelhantes.

KEY WORDS – Hydrogen, isotopic composition, paleoclimate, Cretaceous, Potiguar Basin.

INTRODUCTION

The hydrogen isotopic compositions of sedimentary organic materials are controlled by the D/H ratios of the hydrogen sources used during production of the organic matter, isotopic fractionations associated with metabolism and biosynthesis, and possible isotopic exchanges during diagenetic processes. In the case of algae and higher plants, the source of hydrogen is water (Smith and Epstein, 1970; Estep and Hoering, 1980; Estep and Hoering, 1981). The isotopic composition of water used by non-marine photosynthetic organisms is strongly influenced by geographic location and climate (Craig, 1961; Dansgaard, 1964; Gat 1980). In contrast, the isotopic composition of the water available to marine autotrophs under normal conditions is much less variable (Epstein and Mayeda, 1953). During biosynthesis, the distinct photosynthetic pathways characteristic of C₃, C₄, and CAM plants produce different D/H even for plants grown under identical conditions (Ziegler *et al.*, 1976).

There are divergent opinions about the preservation of hydrogen isotopic compositions in organic materials under geologic conditions. For example, Rigby *et al.* (1981) and Smith *et al.* (1985) suggested that hydrogen exchange was significant in coals during their maturation and during generation of liquid hydrocarbons. However, many other authors found evidence indicating that hydrogen isotopic compositions are mostly preserved in organic materials, as for example in oils as discussed by Yeh and Epstein (1981), Schoell (1984a, 1984b, and 1984c), Peters *et al.*, (1986), Baker (1987), and Burwood *et al.* (1995). Recently, Krishnamurthy *et al.* (1995) observed a covariance between δD values of lacustrine kerogens and climatic variations during the Holocene.

In this paper we describe variations in δD of saturated hydrocarbons in bitumens from lacustrine and marine-evaporitic depositional environments; the inferred relationship between the isotopic compositions of saturated hydrocarbons and of water in paleoenvironments; and the potential use of this approach in paleoclimatic assessment.

BACKGROUND GEOLOGY

The Potiguar Basin is located on the Brazilian equatorial margin and covers an area of approximately 48,000 km², including 21,500 km² onshore (Figure 1). The origin of the basin is associated with the breakup of Gondwanaland, which in this part of South America began in the Aptian-Albian (Asmus and Baisch, 1983; Asmus, 1984; Sztamari *et al.*, 1987). The most prominent

structural features of the onshore Potiguar Basin are three asymmetric half-grabens separated by basement highs and three hinge lines oriented northeast-southwest. The offshore Potiguar Basin has half grabens oriented northwest-southeast that have evolved to a passive marginal basin (Bertani *et al.*, 1990). The geometry of the basin was strongly influenced by a complex network of Proterozoic shear zones produced during the Brazilian/Pan African orogeny (Matos, 1992).

The tectono-stratigraphic evolution of the basin can be divided into three stages: *rift*, *transitional*, and *drift* or *oceanic* (Figure 2). The *rift* stage (Neocomian-Barremian) is characterized by a thick succession of lacustrine fresh water shales and turbidites bordered by progradational deltas (Bertani *et al.*, 1990). Intense tectonism during this stage is indicated by extensive normal and transfer faulting. The end of this stage is marked by a regional unconformity produced by a pre-Aptian tectonic uplift (Bertani *et al.*, 1990). The *transitional* stage (Aptian) is represented by a sequence of carbonates, shales and marls interbedded with deltaic sandstones deposited in a restricted, lagoonal environment with marine influence (Costa *et al.*, 1983). The *drift* or *oceanic* stage (Albian onwards) led to the deposition of two thick sedimentary sequences under open-marine conditions. Firstly, transgressive shales and shelf carbonates covered fluvial sandstones in a shelf-slope system during the Albian to the Turonian and, secondly, from the Campanian to the Holocene, a progradational sequence represented by proximal siliciclastic facies, shallow shelf carbonates, shallow to deep pelites, and turbidites were deposited (Bertani *et al.*, 1990).

SAMPLING

Pendência Formation - Ten rock samples were obtained from a core through a relatively homogeneous shale sequence known as the Livramento Shales, within Sequence III of the Pendência Formation in the well 1 (Lima Neto *et al.*, 1986, Fig. 1). That interval is a regional seismic marker, and may represent the maximum flooding surface of the Pendência Lake (Della Favera *et al.*, 1992). Outside the sampling interval, above and below the Livramento Shale, are found coarser sedimentary facies indicating shallowing of the water level in the Pendência paleolake (Della Favera *et al.*, 1992). Routine micropaleontological examination of the entire lacustrine section in the well 1 has found ostracod-bearing intervals with assemblages typical of the local non-marine stages, Rio da Serra and Aratu (Cenpes/Divex/Sebipe, internal report), which are of Neocomian age.

However, the same examination showed the absence of ostracods in the Livramento Shales.

Alagamar Formation - Fifteen rock samples were taken from a core drilled in the stratigraphic transition from lagoonal to restricted marine in a section of Late Aptian to Early Albian age in well 2 (Fig. 1). This sequence is characterized by a basal succession of carbonates interbedded with sandstones and thin layers of shale and siltstones, in the middle by shales interbedded with carbonates and marls, and at the top by sandstones and shales. Lithostratigraphically, it represents the Ponta do Tubarão beds and the lower part of the Galinhos Member of the Alagamar Formation. Sedimentological and lithological features of both units suggest deposition mostly under lacustrine, deltaic and shallow platform conditions, with sporadic marine incursions (Araripe and Feijó, 1994, Mello *et al.*, 1993, Penteadó, 1995; Vasconcelos, 1995). Micropaleontological examination of the core has yielded mainly pollen and secondarily spores, rare carapaces of conchostraceans, and frequent horizons with large numbers of the ostracods *Cytheridea* (Dino, 1992).

ANALYTICAL TECHNIQUES

Organic Carbon Analysis and "Rock-Eval" Pyrolysis - About 0.5 g of pulverized rock sample was decalcified with HCl (6N) and washed repeatedly with distilled water to eliminate the products of the reaction. The insoluble residue represents mostly clay minerals and total organic carbon. The decalcified samples were analyzed using a Leco WR-12 analyzer, and the resulting measurements of total organic carbon are expressed as a percentage of the whole-rock weight.

Rock-Eval analyses followed the method described by Espitalié *et al.* (1977). The volatiles released during heating at 300°C are represented by S_1 . S_2 (kg HC/t rock) represents the hydrocarbons released from the kerogen during the heating of the sample from 300 to 550°C at 25°C/minute and detected in a flame ionization detector. The temperature of maximum yield of hydrocarbons within S_2 is T_{max} , which provides a measure of the thermal maturity of the preserved organic carbon. S_3 (kg CO₂/t rock) corresponds to CO₂ liberated from kerogen between 300 and 350°C and detected by a thermal conductivity detector. The hydrogen index is given by S_2/TOC and expressed in mg HC/g TOC. The oxygen index is given by S_3/TOC and expressed in mg CO₂/g TOC.

Extraction and column chromatography - Powdered rock samples (30 to 100 g, depending on the hydrocarbon content estimated from the Rock-Eval S_1 peak), were Soxhlet-extracted for 24 h using

dichloromethane (200 ml). After the extraction, the solvent was evaporated and the organic extract transferred to a weighted vial. The saturated and aromatic hydrocarbons and NSO compounds were eluted from a silica-gel column using *n*-hexane, *n*-hexane + dichloromethane (3:2), and methanol, respectively. Only the saturated hydrocarbons were used in this study.

Gas Chromatography and Gas Chromatography/Mass Spectrometry - The saturated hydrocarbons were analyzed using a Hewlett-Packard 5890A gas chromatograph equipped with a splitless injector and a 30-m DB-5 column (Mello, 1988). The carrier gas was hydrogen, and the column temperature was programmed from 40 to 80°C at 8°C/minute and from 80 to 320°C at 4°C/minute. An aliquot of the same sample was analyzed in a HP-5890 mass spectrometer coupled to a Hewlett Packard 5890A GC equipped with an on-column injector and fitted with a 25-m SE-54 column. Helium was used as the carrier gas and the column temperature was programmed from 70 to 190°C at 30°C/minute and from 190 to 290°C at 2°C/minute.

Isotopic Analyses - Saturated hydrocarbons (1 mg) were dissolved in hexane and delivered in a beaker with 1 g of CuO. The solvent was evaporated and the CuO and sample were delivered in a quartz tube (9 mm o.d.) and sealed *in vacuo*. After combustion (2 hours, 850°C), the resulting CO₂ and the H₂O were separated by cryogenic distillation and packaged in sealed 6-mm tubes. The tube that received the water contained about 100 mg of degassed Zn. The hydrogen was obtained after the heating the H₂O + Zn at 500°C for 0.5 h. Both the CO₂ and H₂ were analyzed by mass spectrometry (Finnigan-MAT 252). Carbonates were analyzed isotopically by phosphorolysis *in vacuo* at 25°C. Oxygen isotopic compositions were calculated assuming that all carbonate was calcite and using fractionation factors reported by Rosenbaum and Sheppard (1986). The isotopic compositions of carbon, hydrogen and oxygen are reported, respectively, in $\delta^{13}C$, and δD and $\delta^{18}O$ as per mil deviation from and PDB for carbon and oxygen (Urey *et al.*, 1951) and SMOW for hydrogen (Craig, 1961). The standard deviations of replicate analyses of samples of NBS-22 oil ($\delta^{13}C = -29.81 \pm 0.06\text{‰}$; $\delta D = -119.2 \pm 0.7\text{‰}$; Schoell *et al.*, 1983) were 0.02‰ for carbon (29 analyses) and 1.3‰ for hydrogen (13 analyses).

RESULTS

Organic Carbon and "Rock-Eval" Pyrolysis - Contents of organic carbon in the Livramento Shale of the Pendência Formation vary

from 0.3 to 7.5% (Table I and Fig. 3B). The high percentages (> 70%) of insoluble residue (IR) indicate that clay minerals were abundant in most of the samples (Table I and Fig. 3C). The hydrogen and oxygen indices range from 256 to 772 mg HC/g TOC and 9 to 26 mg CO₂/g TOC, respectively (Table I and Fig. 3D), and indicate that the organic matter is mainly of the types I and II (Espitalié *et al.*, 1977). The hydrocarbon source potential (S₂) varies mostly from good (> 10 kg HC/t rock) to fair (5 < S₂ < 10), and the average T_{max} is = 439°C (Table I and Fig. 4B). The results of Rock-Eval pyrolysis indicate that the examined section of the Pendência Formation is just short of entering the "oil window".

Contents of organic carbon in shales, marlstones and calcilutites from the Alagamar Formation are relatively high and variable within the studied interval, ranging from 2.0 to 12.8% (Table II and Fig. 5B). The distribution of insoluble residues indicates that carbonates (IR < 30%) occur mainly in the lower part of the section, and that shales (IR > 70%) are found mainly in the upper middle of the section (Table II, Fig. 5C). Hydrogen and oxygen indices range from 318 to 663 mg HC/g TOC, and from 9 to 35 mg CO₂/g TOC, respectively, indicating predominance of organic matter of types II and I (Fig. 5D). The average T_{max} of 425°C shows that the section of the Alagamar Formation is thermally immature (Table II and Fig. 6B). The hydrocarbon source potential (S₂) is fair to excellent (6.4 to 79.3 kg HC/ton rock), corroborating the variable quality of the organic matter and the relatively low level of thermal maturity (Table II).

Saturated Hydrocarbons - In the Pendência Formation, gas chromatograms commonly show pristane/phytane > 1, *n*-C₂₃ prominent, high abundances of low molecular weight isoprenoids and β-carotane, and γ-carotane present in most samples (Table III and Fig. 7). As shown in the Figures 8B and 8C, pristane/phytane ratios are relatively invariable and there is a increase in the abundance of β-carotane relative to phytane and *n*-C₂₃ toward the top of the section. In most of the samples, *n*-alkanes with carbon numbers lower than 22 are more abundant than those with carbon numbers higher than 24. Characteristic features found in GC/MS analyses for hopanes (m/z 177 and 191) and steranes (m/z 217 and 218) are higher abundance of Tm, 17a(H), 22,29,30-trisnorhopane, compared with Ts, 18a(H), 22,29,30-trisnorhopane; and gammacerane/C₃₀-hopane ratios with low variations, absent or scarce tetrakishomohopanes and/or pentakishomohopanes; and increasing hopane/sterane ratios toward the top of the section (Table III and Fig. 8C and 8D). The C₂₉ steranes are more abundant than their C₂₈ and C₂₇ counterparts.

In the Alagamar Formation, gas chromatograms of the saturated hydrocarbons indicate greater compositional variations than those found in the Pendência Formation (Table IV and Fig. 9). In most of the samples, pristane/phytane ratios are less than or < 1 or close to unity and branched and cyclic compounds predominate over the *n*-alkanes. In a significant number of the remaining cases, *n*-alkanes with high carbon number (> 22) predominate, and pristane/phytane is greater than 1.0. In other samples, β-carotane and regular *i*-C₂₅ are found. As shown in Figures 10B and 10C, the low pristane/phytane ratios are concentrated in the middle of the section, where pristane and phytane are more abundant than the *n*-alkanes, especially *n*-C₁₇ and *n*-C₁₈. The distribution with depth of hopanes and steranes in the Alagamar section is relatively complex, indicating a dynamic evolution of the paleoenvironment. Some characteristics of the section are very distinctive, for example gammacerane is more abundant than C₃₀-hopane and homohopanes and pentakishomohopanes predominate over tetrakishomohopanes (Fig. 10B). Hopane/sterane ratios are relatively high in the middle of the section (Fig. 10D). Among steranes, C₂₇ and C₂₉ compounds are more abundant than their C₂₈ and C₃₀ counterparts. Diasteranes are generally more conspicuous than in the Pendência Formation.

The ratios of C₂₉ S/(S+R) steranes (Mackenzie *et al.*, 1982) and C₃₁ S/(S+R) hopanes (Ensminger *et al.*, 1977) indicate that the Pendência Formation is slightly more mature than the Alagamar Formation (Tables III and IV). However, both are immature with respect to generation and expulsion of significant amounts of petroleum (the ratios C₂₉ S/(S+R) steranes and C₃₁ S/(S+R) hopanes are lower than 40-44 and 60-62, respectively; Figs. 4C and 4D, and 6C and 6D). In both cases the sections have not yet reached the "oil window" according to calibrations made for the Brazilian marginal basins (Mello, 1988). Thus, the variations in biomarker composition and abundance mainly reflect source inputs.

Isotopic compositions - Values of δD for saturated hydrocarbons in the Pendência Formation seem to vary cyclically, with the lower and upper parts of the section being enriched in D (δD_{sat} > -115‰) relative to the middle of the section (Table V and Fig. 11A). Saturated hydrocarbons in the upper half of the section are mostly depleted in ¹³C (-35.4‰ < δ¹³C < -38.1‰) relative to those in the lower part of the section (-33.4‰ < δ¹³C < -29.5‰; Table V and Fig. 11B). Carbon isotopic compositions of carbonate minerals are relatively constant (0.6 < δ¹³C_{carb} < 1.7‰), suggesting that

the carbon isotopic compositions of dissolved inorganic carbon were relatively constant through time (Table V). Carbonates, which show no petrographic evidence of significant diagenetic alteration, are alternately enriched and depleted in ^{18}O , suggesting variations in the isotopic composition of the water in the paleolake.

In the Alagamar Formation, values of δD for the saturated hydrocarbons reflect increasing depletion from the base of the section ($\cong -115\text{‰}$) to the top of the Ponta do Tubarão beds ($\cong -147\text{‰}$), locally modified by negative spikes ($< -150\text{‰}$). At the base of the Galinhos Member, in the uppermost part of the section, values of $\delta\text{D}_{\text{sat}}$ are $= -149\text{‰} \pm 5\text{‰}$ (Table VI and Fig. 11C). However, the values of $\delta^{13}\text{C}_{\text{sat}}$ indicate cyclic enrichment and depletion in ^{13}C (Table VI and 11D). Santos Neto *et al.* (1996) correlated the positive carbon isotopic excursion in the Alagamar Formation with that of OAE-1 (Arthur and Schlanger, 1979). Thus, global variations in the isotopic composition of marine inorganic carbon may have influenced the isotopic signal of organic carbon of the Alagamar Formation. The values of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ are scattered widely ($-15.8\text{‰} < \delta^{13}\text{C}_{\text{carb}} < -0.5\text{‰}$ and $-9.5\text{‰} < \delta^{18}\text{O}_{\text{carb}} < -1.7\text{‰}$) and suggest significant diagenetic alterations. Dissolution of calcite, cements of various generations, and recrystallized carbonates are observed in thin sections, corroborating the estimate of diagenetic alteration.

DISCUSSION

Significance of Hydrogen Isotopic Compositions in Saturated Hydrocarbons - Hydrogen isotopic variations in the Pendência (-127 to -107‰) and Alagamar Formations (-157 to -110‰) are independent of the compositions and abundances of the saturated hydrocarbons (Figures 8A, 8B, 8C and 8D, and 10A, 10B, 10C and 10D). As shown in Figures 11A, 11B, 11C and 11D, carbon and hydrogen isotopic compositions also vary independently, as would be expected because each is controlled by isotopic compositions of sources which in turn vary independently. For primary producers, water is the source of hydrogen (Smith and Epstein, 1970; Estep and Hoering, 1980; Estep and Hoering, 1981). Consequently, $\delta\text{D}_{\text{sat}}$ must depend on the isotopic composition of the paleoenvironmental water and on isotope effects related to the uptake of water and biosynthesis.

No direct relationship was found between concentrations of D and contents of organic carbon, or lithologic variations, or type of organic matter (Figures 3A, 3B, 3C and 3D, and 5A, 5B, 5C and 5D). Those observations suggest that

bitumens and related oils from carbonate and shale source rocks would have similar δD values if the organic matter had been generated and preserved under similar conditions (identical H sources, equivalent levels of thermal maturity). Correlations observed earlier between deuterium-enriched oils and carbonate source rocks (Schoell 1984a, 1984b and 1984c) probably reflect the relatively drier and warmer paleoclimates associated with carbonate depositional environments.

Isotopic compositions of water in lacustrine settings are directly related to the meteoric water cycle. Thus, $\delta\text{D}_{\text{water}}$ will be influenced by annual mean temperature and amount of monthly precipitation (Dansgaard, 1964), altitude (Payne and Yurtsever, 1974), and distance from the ocean (also known as continentality; Sonntag *et al.*, 1979). In contrast, the isotopic compositions of oceanic waters vary much less strongly (Epstein and Mayeda, 1953; Craig and Gordon, 1965), and, for practical purposes, can be considered nearly constant.

The overall hydrogen isotope effect associated with the uptake of water and with biosynthesis of lipids, measured in fourteen species of modern plants, including five algae, from salt-marsh and lagoonal environments, was found to be $-147 \pm 5\text{‰}$ (Smith and Epstein, 1970). In nine species of microalgae grown under laboratory conditions, the overall hydrogen-isotope effect was found to be $-148 \pm 4\text{‰}$ (Estep and Hoering, 1980). Accordingly, it is suggested that the hydrogen isotopic relationship between water and lipids can be represented in the equation $\delta\text{D}_{\text{lip}} - \delta\text{D}_{\text{water}} \cong -150\text{‰}$. Considering that hydrogen bonded to carbon is relatively unexchangeable (Epstein *et al.*, 1976), it follows that saturated hydrocarbons can serve as proxy indicators of the hydrogen isotopic compositions of paleowaters using the equation $\delta\text{D}_{\text{sat}} - \delta\text{D}_{\text{water}} \cong -150\text{‰}$.

In the examined lacustrine and marine-evaporitic sections there is no evident relationship between $\delta\text{D}_{\text{sat}}$ and T_{max} or between $\delta\text{D}_{\text{sat}}$ and other indicators of maturity (Figs. 4A, 4B, 4C and 4D, and 6A, 6B, 6C and 6D). The T_{max} values found for the Pendência (434°C to 447°C) and Alagamar Formations (415°C to 440°C , Tables I and II) are in the same range of those inferred for intense smectite-illite diagenesis ($\cong 430\text{°C}$ to 440°C , Burtner and Warner, 1986). Apparently, as proposed by Yeh and Epstein (1981) and Schoell (1984b) and contrary to the suggestion of Clayton (1983), there is no significant hydrogen-isotopic exchange between organic material and water released by the dehydration of smectite in the Pendência and Alagamar samples.

However, clay minerals can provide evidence about the hydrogen isotopic compositions of waters in the paleoenvironments that they were formed

(Savin and Epstein, 1970). This will be checked in future studies using rock samples with clay minerals with different diagenetic levels in the Potiguar Basin.

Paleoenvironmental Changes and Related Variations in δD_{sat} - The Pendência Formation is comprised of lacustrine, deltaic, and fan-deltaic sediments (Bertani *et al.*, 1990) that reach maximum thickness of about 6,000 m in the deepest parts of the Potiguar grabens (Neves, 1989). As is typical in lacustrine sequences, the organic geochemical characteristics vary significantly, and there are intervals that yield oil and gas in commercial amounts (Rodrigues *et al.*, 1983; Mello *et al.*, 1984).

Expansions and contractions in lakes, with consequent variations in salinity, are common because climate changes can produce immediate and drastic changes in conditions of deposition (Kelts, 1988). Most of the organic-rich shales of the Pendência Formation have geochemical features that have been attributed to deposition under fresh water conditions. For example, $\delta^{13}C < -28.0\%$, sulfur contents $< 0.1\%$, *n*-alkanes maximizing at C_{21}/C_{23} , pristane/phytane ratios > 1.3 , hopane/sterane ratios < 6.0 , gammacerane index < 50 , tricyclic index 3-126, bisnorhopane index < 5 , and *i*- $C_{25} + i$ - $C_{30} < 370$ ppm (Mello *et al.*, 1988a; Mello *et al.*, 1990; Trindade *et al.*, 1992). However, more recently, Mello *et al.* (1993) recognized intervals in the Pendência shales with geochemical characteristics attributable to hypersaline conditions. For example, hopane/sterane and pristane/phytane ratios are relatively lower; β -carotane is abundant, as are *i*- C_{25} and *i*- C_{30} ; shorter-chain *n*-alkanes ($< n$ - C_{20}) are predominant; homohopanes (C_{31} - C_{35}) are present, with C_{35} predominant over C_{34} ; and C_{30} steranes (24-*n*-propylcholestanes, m/z 414 \rightarrow 217) and dinosteranes (m/z 414 \rightarrow 98) are absent. Such changes would be expected to affect hydrogen-isotopic compositions of source waters.

The values of δD_{sat} of the Pendência Formation are distributed in two cycles of positive-negative excursions that may reflect climatic fluctuations. Using the equation $\delta D_{sat} - \delta D_{water} \cong -150\%$, the values of δD_{water} estimated for the Pendência paleolake varied from about 23‰ to 43‰ vs. SMOW during the periods of minimum and maximum aridity, respectively. Such values of δD_{water} represent enrichments in D that are compatible with those presently found in water bodies subject to intense evaporation under warm and semi-arid conditions, for example in lakes and rivers of the Northern Kalahari, Botswana Africa ($\delta D_{water} \cong 40$ to 60‰; Mazor *et al.*, 1977), or in the Lake Chad (total area of about 20,000 km²) in Central Africa where δD_{water} can reach $\cong 110\%$ in its northwestern part (Pearson and Coplen, 1978).

Conclusions drawn from other lines of evidence are in agreement with these isotopically based estimates. Paleoclimatic reconstructions for the northern Gondwana rift lakes during the early Cretaceous indicate warm climate with alternating negative and positive net precipitation seasons (Moore *et al.*, 1995). Local studies using pollen assemblages have found, in Sequence III of the Pendência Formation, evidence for a tropical to subtropical climate with periods of variable humidity (Picarelli and Lana, 1993). Despite the fluctuations in δD_{sat} , there is a general trend of enrichment in D from the bottom toward the top of the studied core, and this may indicate a long-term trend of increasing dryness during deposition of the younger portions of the Livramento shales. As shown in Figures 8B and 8C, the higher abundances of β -carotane in the upper part of the section suggest increasing aridity and/or salinity in the Pendência paleolake (Hall and Douglas, 1983; Mello *et al.*, 1988a; Carroll *et al.*, 1992). High hopane/sterane ratios were interpreted as reflecting increased salinity in lacustrine paleoenvironments in the Brazilian marginal basins (Mello and Maxwell, 1990), and this fits with the continuous increase of hopane/sterane ratios toward the top of the section (Fig. 8D). Rodrigues and Takaki (1992) and Rodrigues *et al.* (1993), using $\delta^{18}O_{carb}$ and pollen assemblages, suggested variable and increased salinity levels in the paleoenvironment evolving toward deposition of the shales overlying the Livramento Shales. Not surprisingly, the values of δD_{water} in the examined lacustrine section are similar to those found in modern lakes under comparable climatic conditions. These observations suggest that the estimated overall hydrogen isotope effect relating water to saturated hydrocarbons, and the inferred values of δD for the water in the paleoenvironment, are significant.

The values of $\delta^{18}O_{carb}$ in the Pendência Formation should also reflect, at least in part, the variations in the isotopic composition of the paleolake water. Higher and lower $\delta^{18}O_{carb}$ values must denote varying losses of ¹⁶O from the paleolake due to evaporation of water in periods of higher or lower aridity, respectively (Stuiver, 1970; Talbot, 1990). As shown in Figure 12, δD_{sat} and $\delta^{18}O_{carb}$ have comparable trends. However, they are not precisely covariant, suggesting that hydrogen and oxygen isotopic variations of water are not recorded synchronously by δD_{sat} and $\delta^{18}O_{carb}$ (for example, due to the influence of pore waters on $\delta^{18}O_{carb}$), or that both can be influenced differently by the same paleoenvironmental conditions.

In the Alagamar Formation (Ponta do Tubarão beds and Galinhos Member), the sedimentological and stratigraphic characteristics

are typical of transitional environments in which non-marine and marine features coexist. The Ponta do Tubarão beds contain a lithologic assemblage typical of supratidal carbonates and evaporites deposited in marginal sabkhas, and the Galinhos shales represent a condensed section that must record the apex of the Aptian transgression in the Potiguar Basin (Vasconcelos, 1995). The complexity of those paleoenvironments is evident in paleontological studies that are not unanimous in estimates of marine influences on the Aptian sediments. However, Regali and Gonzaga (1982, 1985) suggested that the sediments corresponding to the local stage "Alagoas", which is correlated with the international Aptian stage, were deposited synchronously under continental and marine conditions. Specific fossil assemblages strongly suggest marine influence in the Late Aptian-Early Albian interval of the Alagamar Formation. For example, spores, chitin carapaces of foraminifera, dinoflagellates, and acritarchs are associated (Regali, 1986), as are dinoflagellates of the genus *Subtilisphaera*, chitin carapaces of foraminifera, and rare microgastropods (Regali, 1986, Arai *et al.*, 1994).

Marine influences on the Aptian source rocks and related oils in both the onshore (Rodrigues *et al.*, 1983) and offshore Potiguar Basin (Mello *et al.*, 1984, 1988a, 1988b) have long been recognized. The marine influence may have occurred in a restricted, long and narrow lagoon under arid to semi-arid climate that enhanced the salinity of the water, suggesting not just marine, but rather marine-evaporitic conditions. Among the characteristic geochemical features found in the Alagamar source rocks and their correlated oils are predominance of *n*-alkanes with low molecular weights, low pristane/phytane ratios, relatively high concentrations of *i*-C₂₅ (2,6,10,14,18-pentamethyleicosane) and *i*-C₃₀ (squalane), presence of β -carotane and 28,30-bisnorhopane in variable concentrations, high gammacerane/C₃₀ hopane ratios, high homohopane index, and Ts/Tm ratios < 1. Most recently, C₃₀ steranes (24-*n*-propylcholestanes) and dinosteranes were found in organic extracts of the Ponta do Tubarão beds and Galinhos Member of the Potiguar Basin, corroborating other evidence for marine influence during that interval (Mello *et al.*, 1993; Penteado, 1995; and Vasconcelos, 1995). *n*-Propylcholestane has been attributed to marine algae of the family *Chrysophyta* (Moldowan *et al.*, 1985; Moldowan *et al.*, 1990) and dinosteranes derive from marine dinoflagellates (Summons *et al.*, 1987; Summons *et al.*, 1992). The heterogeneity of the paleoenvironment is reflected in the high variabilities in the composition and abundance of

specific biomarker in the Alagamar Formation (Figs. 10B, 10C and 10D). Variations in levels of O₂, stratification, and salinity appear to have been significant in the Alagamar paleolagoon. For example, the very low pristane/phytane ratios (<0.6), together with the relatively high gammacerane/C₃₀-hopane ratios, suggest an decrease in the availability of O₂ and enhancement of salinity in the middle of the section (Mello *et al.*, 1988a; Peters and Moldowan, 1993). Contrasting densities between waters from marine incursions and the denser hypersaline waters of the lagoon would facilitate stratification and anoxic conditions as well (Mello *et al.*, 1993).

Saturated hydrocarbons in the Alagamar Formation trend toward depletion in deuterium from the Ponta do Tubarão beds towards the Galinhos Member, at the top of the section (Fig. 5A). Those results are in agreement with the expected evolution of a lagoon, with a restricted outlet to open ocean, evolving to less restricted conditions under a warm and semi-arid climate and subject to episodic marine incursions (Mello *et al.*, 1993). In the lower part of the section, below 1255 m, the saturated hydrocarbons are significantly enriched in D, suggesting that the producers used a D-enriched source. The equation $\delta D_{\text{sat}} - \delta D_{\text{water}} \cong -150\text{‰}$ suggests that the δD_{water} in that paleoenvironment ranged from about 15 to 40‰. Those values are compatible with a variety of waters from continental (Mazor, 1977; Mazor, 1991; Salati *et al.*, 1980) and littoral environments (Swart *et al.*, 1989) at low latitudes and altitudes in warm climates with variable humidity levels.

Negative spikes in the δD_{sat} record could represent marine incursions, and the establishment of predominantly marine conditions appears to have occurred in the upper part of the Ponta do Tubarão beds, above \cong 1230 m where values of δD_{sat} vary around -150‰ (Fig. 5A). That is a value expected for lipids produced by photosynthetic organisms relying on a hydrogen source (water) with δD around 0‰ suggesting marine influence on the depositional environment of the upper part of the Ponta do Tubarão beds and base of the Galinhos Member. Global paleogeographic reconstructions suggest that small changes in the geographic position of the Potiguar Basin occurred from the mid-Cretaceous to the present (Scotese *et al.*, 1989). Since formation of the Potiguar Basin in the Early Neocomian, Northeastern Brazil has experienced only pull-apart tectonics (Mello, 1987). Therefore, stronger negative shifts in δD_{sat} could not be explained by cooler temperatures (altitude effect) or melting of glaciers from hypothetical highlands in the surroundings. There are two samples, at 1214.3 m and 1230.8 m, with values of

δD_{sat} significantly lower than -150‰ , namely -154 and -157‰ , respectively. Two possible explanations can be suggested for these high depletions in D. One is that the isotopic composition of seawater during the Aptian was equal to that at present but that isotopic fractionations associated with primary production in the Alagamar paleolagoon were larger than 150‰ . However, there are no reports in studies of modern biota of fractionations as large as 160‰ . Alternatively, the mid-Cretaceous oceans would have been isotopically lighter than today's oceans, and the overall hydrogen isotope effect would still have been $\approx -150\text{‰}$. This second possibility is more likely, since the mid-Cretaceous was characterized by a global greenhouse episode coincident with high rates of oceanic crust production and high sea level (Larson, 1995). During such periods of global warmth, if the highly D-depleted polar ice and glaciers were to melt at least in part, the δD of the oceans would decrease. Relevant faunal and floral data corroborate the warmer and more equable climate during the mid-Cretaceous compared with today's climate (Barron, 1983; Crowley 1983). Thus, δD_{sat} values of the Alagamar Formation can be explained and are compatible with the complex evolution of the mid-Cretaceous transitional environment of the Potiguar Basin, under the inferred local and global climatic conditions of that time.

CONCLUSIONS

The hydrogen isotopic compositions of saturated hydrocarbons from the bitumens examined here are largely independent of the content of organic carbon, type of organic matter, and lithology of the host rock, suggesting that most of the variations in δD_{sat} are primary. Although the values of T_{max} in the sections are in the range expected to be associated with intense smectite-illite diagenesis ($430 - 440^\circ\text{C}$, Burtner and Warner, 1986), evidence for exchange of hydrogen isotopes between saturated hydrocarbons or their precursors and water is absent, indicating preservation of hydrogen isotopic compositions at these levels of thermal maturity.

The cyclic variations of δD_{sat} found in lacustrine shales from the Pendência Formation suggest fluctuations in the δD_{water} of the paleolake, probably due to periodic climatic changes. The observed enrichments and depletions of D plausibly reflect periods of lower and higher humidities, respectively, as expected for the paleoclimatic conditions inferred for the region during the mid-Cretaceous.

In contrast, the δD_{sat} values in the Alagamar

Formation decline steadily from the Ponta do Tubarão beds toward the Galinhos Member at top of the section. This trend is consistent with evolution of the paleoenvironment, under semi-arid to arid conditions, from a long and narrow lagoon to a more open environment with enhanced marine influence. Negative spikes in the δD_{sat} record probably represent the most significant marine incursions in the Alagamar paleolagoon.

The inferred hydrogen isotopic compositions of the water in the examined paleoenvironments, which were estimated from the relationship $\delta D_{\text{sat}} - \delta D_{\text{water}} \approx -150\text{‰}$, are compatible with δD_{water} found in modern environments under similar climatic conditions. These results suggest consistency of the overall hydrogen isotopic fractionation between water and lipids and the preservation of the original isotopic signal in saturated hydrocarbons.

The results of this study suggest that δD_{sat} from bitumens with relatively low levels of thermal maturity can be used to assess paleoclimatic conditions in the Potiguar Basin, and probably in other marginal basins from Brazil and West Africa. The reliability of the interpretations using δD_{sat} is significantly enhanced by integration with geochemical, geological, and paleontological information. Caution must be exercised in interpretation of the hydrogen isotopic compositions of other bitumens with significantly higher degrees of thermal maturity.

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Table I
Total Organic Carbon, Insoluble Residue, and Results of "Rock-Eval" Pyrolysis, of the Pendência Formation

| depth (m) | TOC (%) | IR (%) | S ₂ kg HC/t rock | Tmax (°C) | HI mgHC/gTOC | OI mgCO ₂ /gTOC |
|--------------|------------|-----------|--------------------------------|--------------|-----------------|-------------------------------|
| 1484.40 | 0.3 | 76 | n.d. | n.d. | n.d. | n.d. |
| 1484.90 | 0.7 | 76 | 1.7 | 447 | 256 | 26 |
| 1486.40 | 2.0 | 73 | 12.5 | 444 | 616 | 14 |
| 1487.50 | 2.7 | 72 | 17.8 | 439 | 657 | 15 |
| 1489.55 | 2.5 | 73 | 15.5 | 440 | 629 | 13 |
| 1490.05 | 1.6 | 68 | 4.2 | 434 | 261 | 24 |
| 1492.05 | 7.5 | 80 | 58.1 | 440 | 772 | 9 |
| 1493.65 | 2.9 | 84 | 20.5 | 438 | 699 | 10 |
| 1495.25 | 1.7 | 73 | 8.4 | 434 | 504 | 21 |
| 1496.85 | 1.0 | 76 | 3.5 | 438 | 340 | 41 |

n.d. not determined

Table II
Total Organic Carbon, Insoluble Residue, and Data from "Rock-Eval" Pyrolysis of the Alagamar Formation

| depth (m) | TOC (%) | IR (%) | S ₂ kg HC/t rock | Tmax (°C) | HI mgHC/gTOC | OI mgCO ₂ /gTOC |
|--------------|------------|-----------|--------------------------------|--------------|-----------------|-------------------------------|
| 1212.4 | 2.3 | 84 | 10.1 | 434 | 440 | 17 |
| 1214.3 | 3.9 | 80 | 20.3 | 440 | 517 | 9 |
| 1216.4 | 5.4 | 80 | 30.6 | 436 | 565 | 10 |
| 1218.3 | 3.4 | 84 | 15.2 | 429 | 450 | 14 |
| 1222.2 | 12.8 | 72 | 79.3 | 424 | 620 | 26 |
| 1228.6 | 4.3 | 80 | 15.7 | 416 | 369 | 19 |
| 1230.8 | 2.0 | 72 | 6.4 | 420 | 318 | 27 |
| 1239.4 | 3.5 | 72 | 15.0 | 417 | 424 | 21 |
| 1240.6 | 8.1 | 24 | 46.6 | 420 | 573 | 18 |
| 1244.3 | 3.6 | 76 | 17.3 | 421 | 477 | 18 |
| 1247.3 | 8.1 | 68 | 44.3 | 425 | 546 | 19 |
| 1256.6 | 2.5 | 19 | 16.6 | 422 | 663 | 25 |
| 1262.7 | 4.0 | 60 | 26.0 | 435 | 654 | 19 |
| 1273.7 | 2.4 | 19 | 12.4 | 427 | 509 | 35 |
| 1285.3 | 4.5 | 84 | 21.6 | 415 | 482 | 20 |

Table III
Ratios of Selected Saturated Hydrocarbons of the Pendência Formation

| Depth (m) | Pristane/ Phytane | β -carot./ <i>n</i> -C ₂₃ | Phytane/ β -Carotane | Ts/ (Ts+Tm) | Hopane/ Sterane | Gammac./ C ₃₀ Hop. | C ₂₉ /C ₂₈ Steranes ($\beta\beta$) | C ₃₁ S/(S+R) Homohop. | C _{29$\alpha\alpha\alpha$} S/(S+R) Steranes |
|-----------|----------------------|---|-------------------------------|----------------|--------------------|----------------------------------|--|--|---|
| 1484.40 | 1.54 | 0.31 | 1.06 | 0.28 | 22.8 | 0.24 | n.d. | 0.58 | 0.41 |
| 1484.90 | 1.54 | 0.80 | 0.51 | 0.30 | 13.0 | 0.37 | 1.22 | 0.56 | 0.43 |
| 1486.40 | 1.78 | 0.74 | 0.50 | 0.22 | 17.7 | 0.34 | 1.21 | 0.56 | 0.43 |
| 1487.50 | 1.55 | 0.68 | 0.66 | 0.18 | 15.8 | 0.25 | 1.33 | 0.55 | 0.43 |
| 1489.55 | 1.47 | 0.74 | 0.79 | 0.19 | 17.3 | 0.25 | 1.41 | 0.55 | 0.42 |
| 1490.05 | 1.40 | 0.40 | 1.10 | 0.23 | 7.2 | 0.35 | 1.26 | 0.52 | 0.44 |
| 1492.05 | 1.49 | 0.26 | 2.17 | 0.22 | 10.0 | 0.45 | 1.26 | 0.53 | 0.43 |
| 1493.65 | 1.21 | 0.36 | 1.31 | 0.24 | 4.3 | 0.40 | 1.19 | 0.53 | 0.42 |
| 1495.25 | 1.27 | 0.14 | 2.33 | 0.17 | 7.6 | 0.28 | 1.34 | 0.56 | 0.43 |
| 1496.85 | 1.26 | 0.31 | 1.59 | 0.17 | 5.3 | 0.43 | 1.35 | 0.55 | 0.44 |

Table IV
Ratios of Selected Saturated Hydrocarbons of the Alagamar Formation

| Depth (m) | Pristane/ Phytane | Pristane/ <i>n</i> -C ₁₇ | Phytane/ <i>n</i> -C ₁₈ | Ts/ (Ts+Tm) | Hopane/ Sterane | Gammac./ C ₃₀ Hop. | C ₂₉ /C ₂₈ Steranes | C ₃₁ S/(S+R) Homohop. | C _{29$\alpha\alpha\alpha$} S/(S+R) Steranes |
|--------------|----------------------|--|---------------------------------------|----------------|--------------------|----------------------------------|--|--|---|
| 1212.4 | 1.63 | 1.63 | 1.09 | 0.31 | 3.1 | 1.41 | 0.87 | 0.40 | 0.31 |
| 1214.3 | 2.60 | 0.68 | 0.37 | 0.15 | 11.3 | 0.35 | 0.62 | 0.32 | 0.32 |
| 1216.3 | 1.48 | 0.96 | 0.77 | 0.32 | 4.7 | 0.57 | 0.57 | 0.37 | 0.22 |
| 1218.3 | 0.64 | 1.35 | 2.28 | 0.38 | 0.7 | 1.54 | 0.78 | 0.46 | 0.22 |
| 1222.2 | 1.13 | 4.87 | 4.98 | 0.36 | 1.7 | 0.22 | 1.22 | 0.42 | 0.21 |
| 1228.6 | 0.82 | 6.86 | 7.70 | 0.31 | 0.6 | 0.61 | 2.40 | 0.41 | 0.17 |
| 1230.8 | 0.49 | 5.28 | 9.45 | 0.24 | 0.6 | 0.40 | 1.64 | 0.38 | 0.18 |
| 1239.4 | 0.60 | 1.17 | 12.62 | 0.41 | 0.4 | 0.89 | 3.70 | 0.44 | 0.22 |
| 1240.6 | 0.61 | 2.14 | 6.12 | 0.35 | 0.6 | 1.44 | 1.36 | 0.48 | 0.19 |
| 1244.3 | 0.43 | 2.18 | 10.44 | 0.42 | 0.4 | 1.50 | 5.42 | 0.42 | 0.30 |
| 1247.3 | 0.49 | 1.93 | 4.52 | 0.31 | 0.6 | 1.25 | 0.95 | 0.38 | 0.20 |
| 1256.6 | 0.44 | 6.29 | 12.56 | 0.33 | 0.5 | 0.29 | 1.40 | 0.41 | 0.25 |
| 1262.7 | 1.96 | 0.70 | 0.42 | 0.28 | 7.7 | 0.12 | 1.00 | 0.37 | 0.33 |
| 1273.7 | 1.83 | 2.03 | 1.51 | 0.29 | 12.0 | 0.19 | 0.47 | 0.45 | 0.25 |
| 1285.3 | 1.45 | 2.55 | 1.79 | 0.23 | 0.8 | 0.76 | 0.53 | 0.40 | 0.17 |

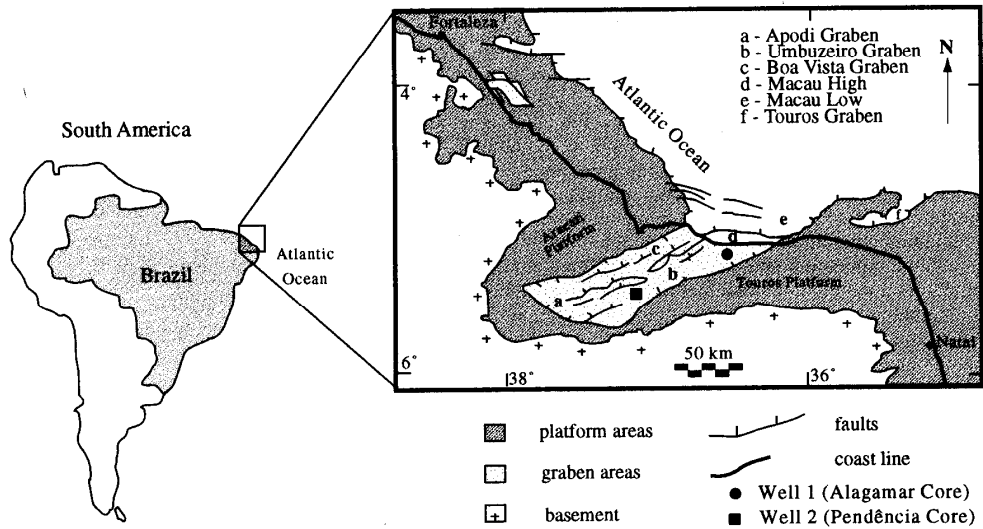
Table V
Isotopic Compositions of Carbon and Hydrogen of Saturated Hydrocarbons and Carbon and Oxygen of Carbonate Fraction of the Pendência Formation

| depth (m) | $\delta^{13}\text{C}_{\text{sat}}$ (‰) | $\delta\text{D}_{\text{sat}}$ (‰) | $\delta^{13}\text{C}_{\text{carb}}$ (‰) | $\delta^{18}\text{O}_{\text{carb}}$ (‰) |
|--------------|---|--------------------------------------|--|--|
| 1484.40 | -31.8 | -107 | 1.0 | -5.6 |
| 1484.90 | -35.4 | -119 | 1.1 | -6.9 |
| 1486.40 | -36.1 | -112 | 1.2 | -7.2 |
| 1487.50 | -35.9 | -107 | 1.7 | -6.8 |
| 1489.55 | -36.3 | -126 | 1.2 | -5.7 |
| 1490.05 | -36.1 | -127 | 0.6 | -8.1 |
| 1492.05 | -38.1 | -127 | 0.8 | -8.8 |
| 1493.65 | -33.4 | -123 | 0.5 | -6.4 |
| 1495.25 | -29.5 | -112 | 0.7 | -6.2 |
| 1496.85 | -32.3 | -115 | 0.2 | -5.3 |

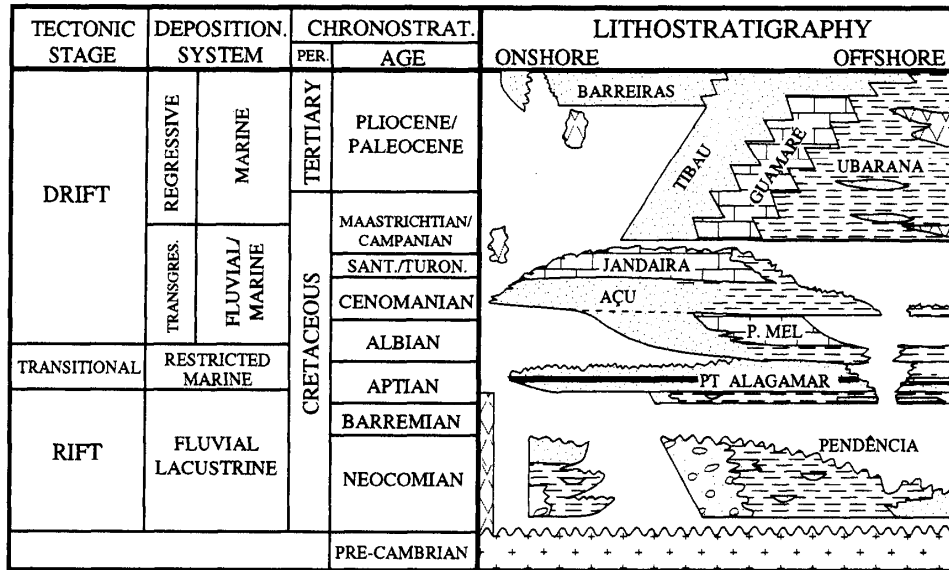
Table VI
Isotopic Compositions of Carbon and Hydrogen of Saturated Hydrocarbons
and Carbon and Oxygen of Carbonate Fraction of the Alagamar Formation

| depth (m) | $\delta^{13}\text{C}_{\text{sat}}$ (‰) | $\delta\text{D}_{\text{sat}}$ (‰) | $\delta^{13}\text{C}_{\text{carb}}$ (‰) | $\delta^{18}\text{O}_{\text{carb}}$ (‰) |
|--------------|---|--------------------------------------|--|--|
| 1212.4 | -27.6 | -144 | -2.0 | -3.4 |
| 1214.3 | -29.6 | -154 | n.d. | n.d. |
| 1216.3 | -29.4 | -148 | -7.2 | -1.7 |
| 1218.3 | -26.4 | -150 | -15.8 | -8.5 |
| 1222.2 | -27.4 | -147 | -12.2 | -7.9 |
| 1228.6 | -23.5 | -135 | -6.9 | -4.0 |
| 1230.8 | -21.4 | -157 | -2.5 | -9.5 |
| 1239.4 | -23.89 | -140 | 7.2 | -9.1 |
| 1240.6 | -25.8 | -147 | -5.7 | -7.9 |
| 1244.3 | -27.0 | -138 | -0.5 | -2.9 |
| 1247.3 | -27.1 | -146 | -10.9 | -3.0 |
| 1256.6 | -25.9 | -135 | -8.3 | -9.2 |
| 1262.7 | -29.6 | -131 | -0.9 | -2.1 |
| 1273.7 | -27.5 | -116 | -0.5 | -8.6 |
| 1285.3 | -23.8 | -110 | -4.1 | -6.8 |

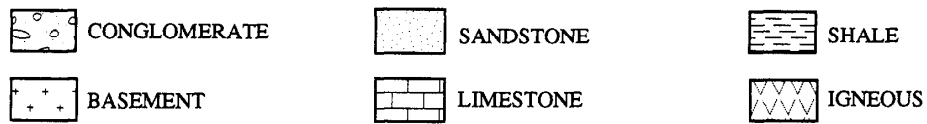
n.d. not determined



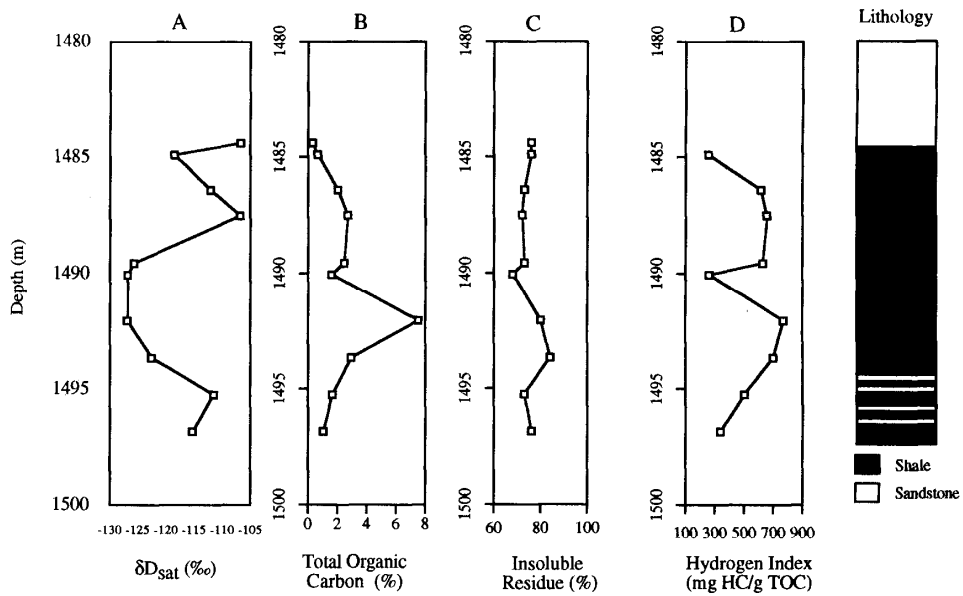
1 - Location map for the Potiguar Basin



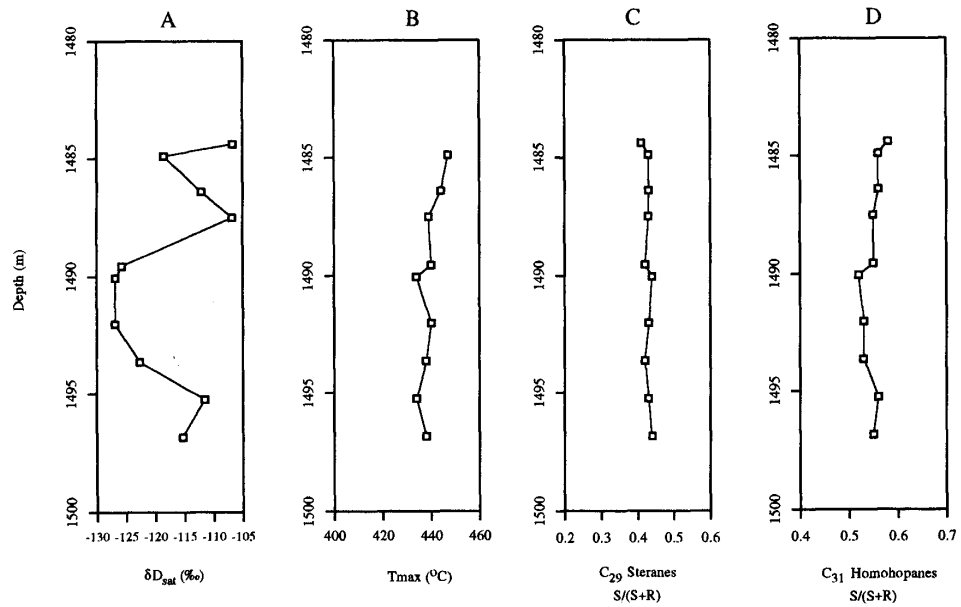
Araripe and Feijó (1994)



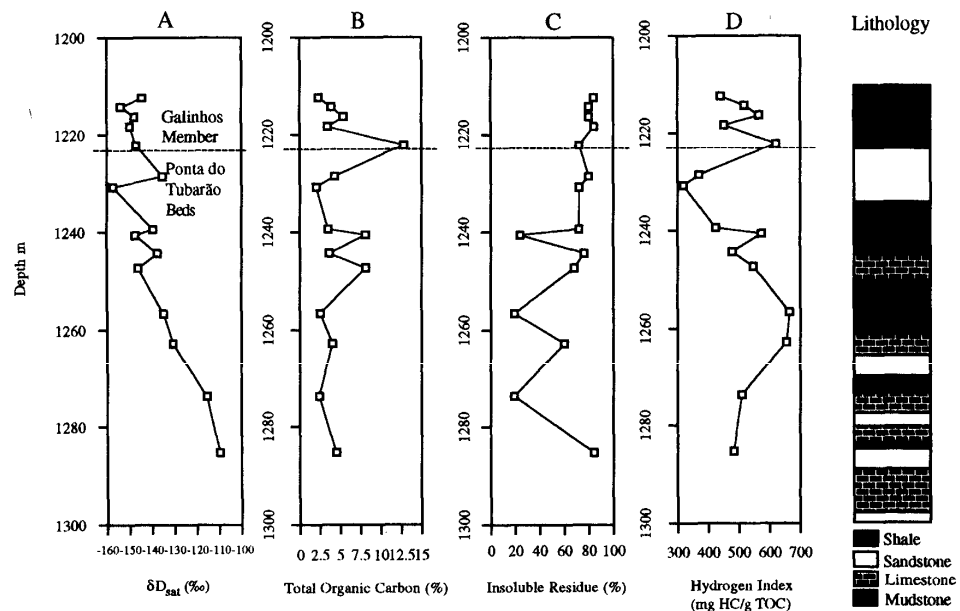
2 - Stratigraphic chart for the Potiguar Basin



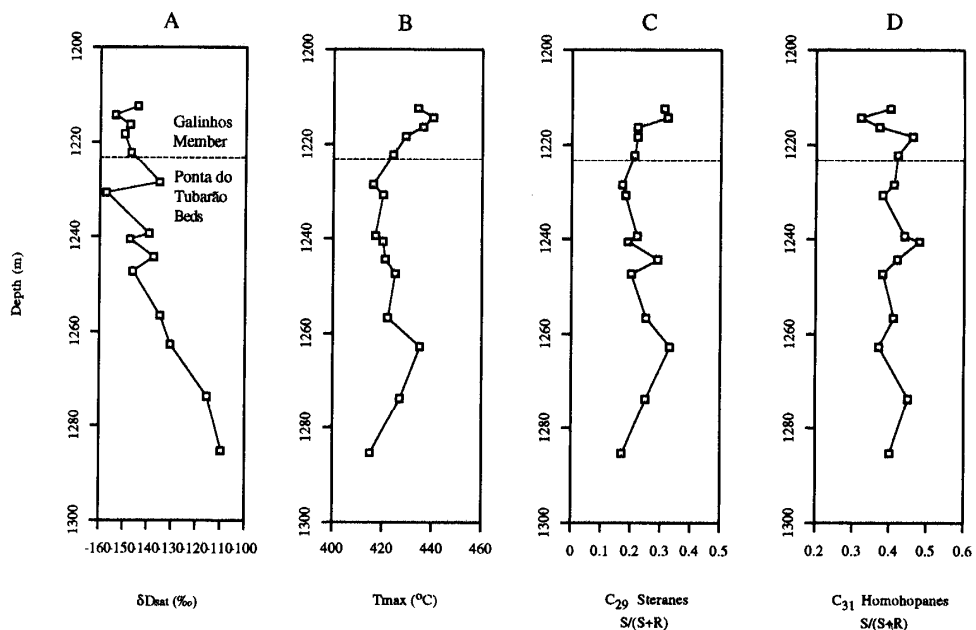
3 - δD_{sat} vs. depth (A), total organic carbon vs. depth (B), insoluble residue vs. depth (C), hydrogen index vs. depth (D), Pendência Formation



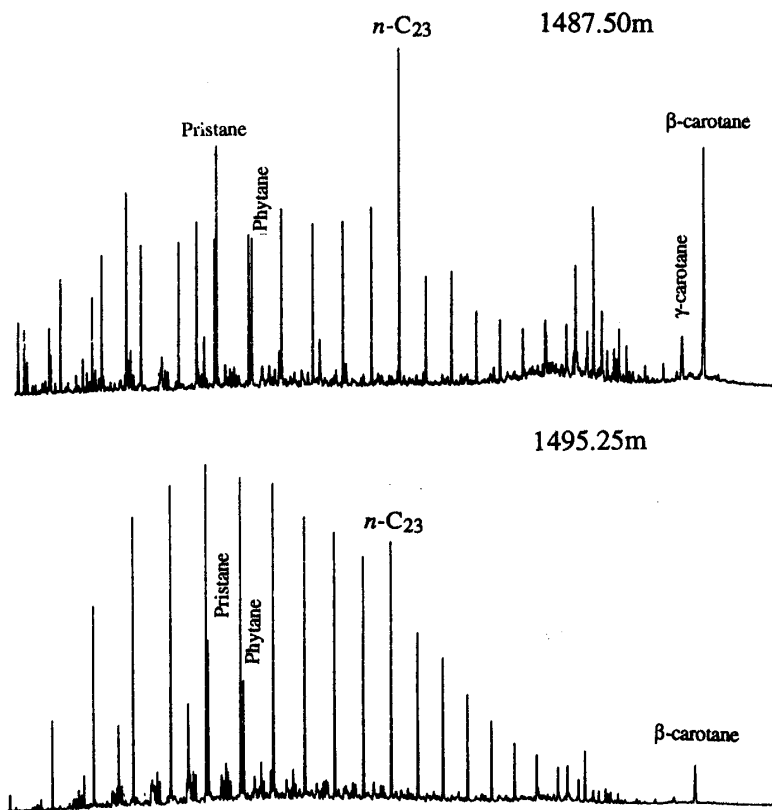
4 - δD_{sat} vs. depth (A), T_{max} vs. depth (B), C_{29} S/(S+R) steranes vs. depth (C), C_{31} S/(S+R) homohopanes vs. depth (D), Pendência Formation



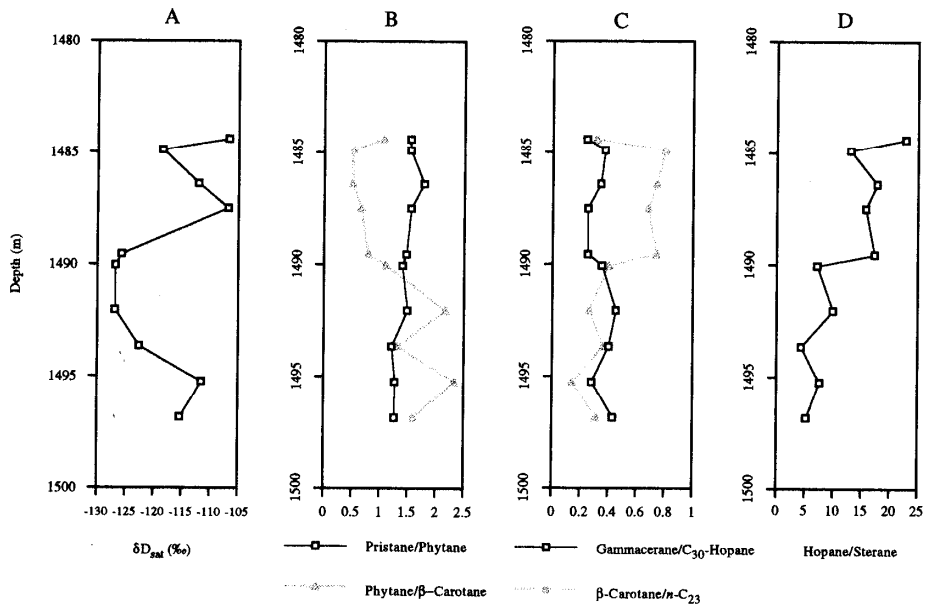
5 - δD_{sat} vs. depth (A), total organic carbon vs. depth (B), insoluble residue vs. depth (C), hydrogen index vs. depth (D), Alagamar Formation. The dashed line is the contact between Ponta do Tubarão beds and Galinhos Member (top)



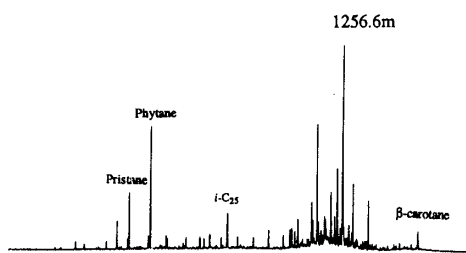
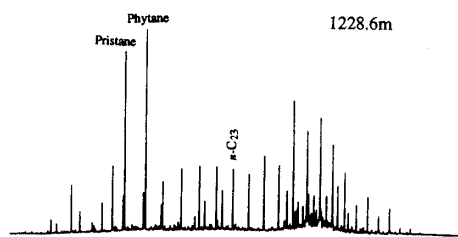
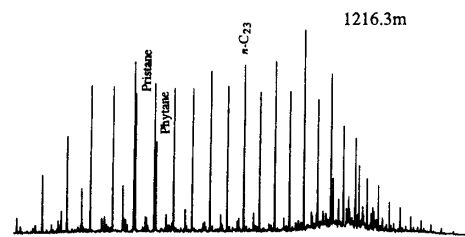
6 - δD_{sat} vs. depth (A), T_{max} vs. depth (B), C_{29} S/(S+R) steranes vs. depth (C), C_{31} S/(S+R) homohopanes vs. depth (D), Alagamar Formation. The dashed line is the contact between Ponta do Tubarão beds and Galinhos Member (top)



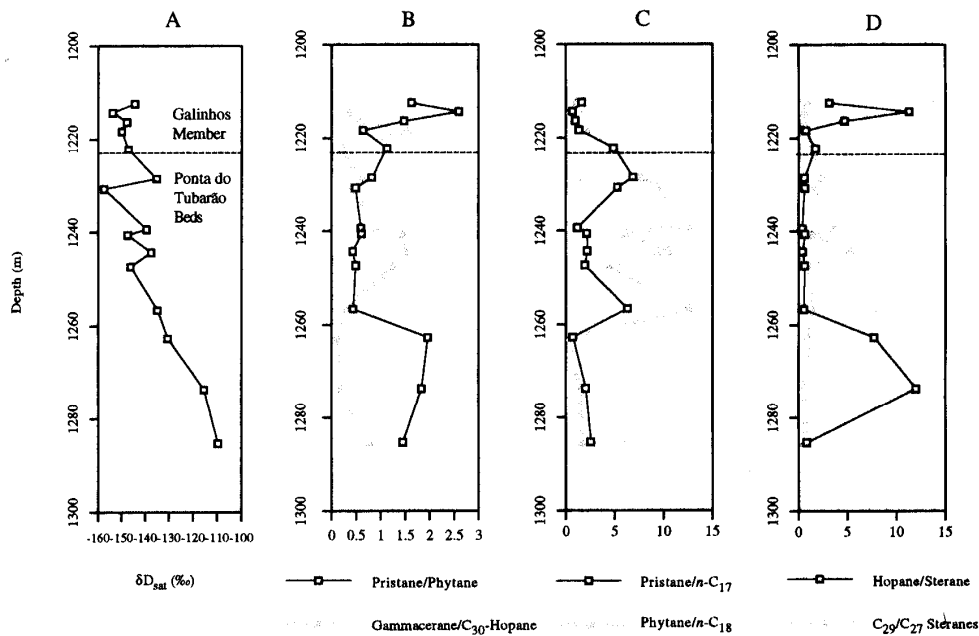
7 - Gas chromatograms of saturated hydrocarbons from the Pendência Formation



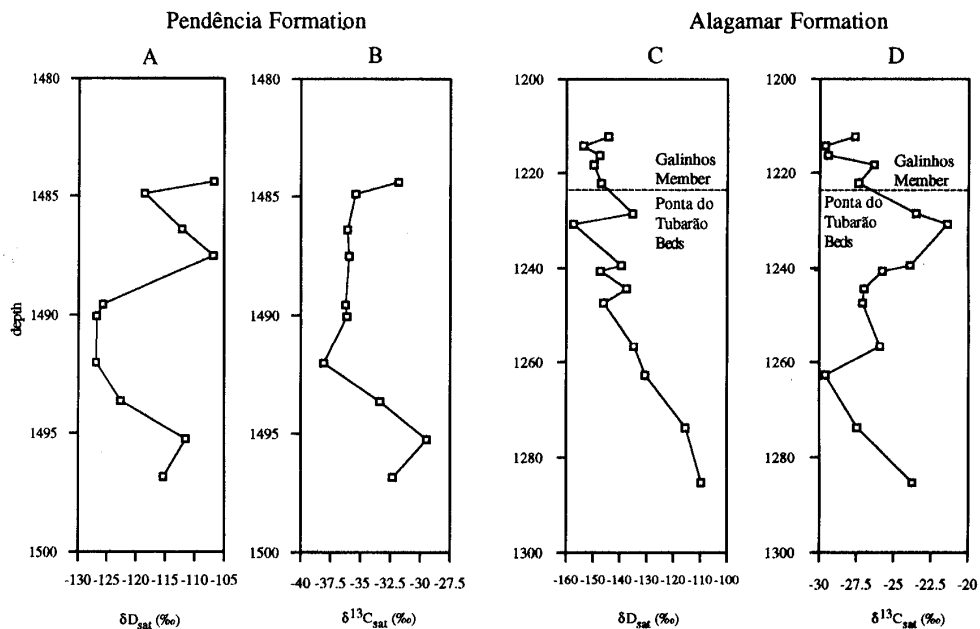
8 - δD_{sat} vs. depth (A), pristane/phytane and phytane/ β -carotane ratios vs. depth (B), gammacerane/ C_{30} -hopane and β -carotane/ n - C_{23} ratios vs. depth (C), hopane/sterane ratio vs. depth (D), Pendência Formation



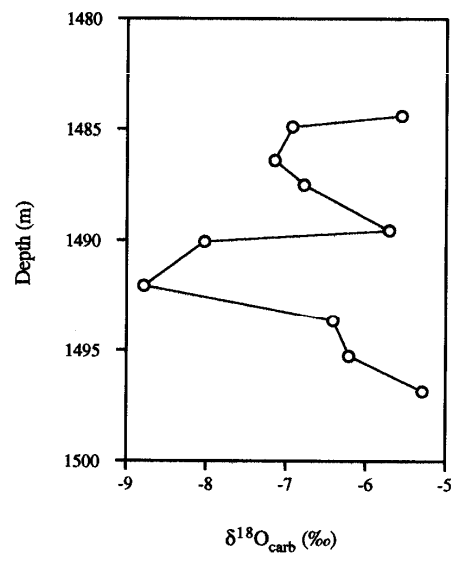
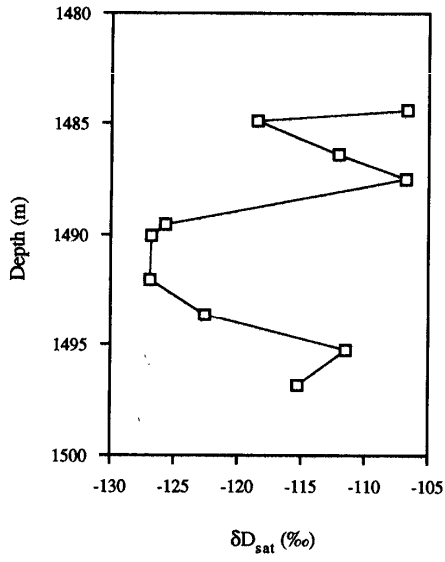
9 - Gas chromatograms of saturated hydrocarbon from the Alagamar Formation



10 - δD_{sat} vs. depth (A), pristane/phytane and gammacerane/ C_{30} -hopane ratios vs. depth (B), pristane/ $n-C_{17}$ and phytane/ $n-C_{18}$ ratios vs. depth (C), hopane/sterane and C_{29}/C_{27} sterane ratios vs. depth (D), Alagamar Formation. The dashed line is the contact between Ponta do Tubarão beds and Galinhos Member (top).



11 - δD_{sat} vs. depth (A), $\delta^{13}C_{sat}$ vs. depth (B), Pendência Formation; δD_{sat} vs. depth (C), $\delta^{13}C_{sat}$ vs. depth (D), Alagamar Formation. The dashed line is the contact between Ponta do Tubarão beds and Galinhos Member (top)



12 - $\delta^{13}C_{sat}$ and $\delta^{18}O_{carb}$ vs. depth, Pendência Formation